A Volumetric Analysis (Complexometric Titration) of Calcium in Hard Water

In this laboratory exercise, we will analyze an unknown powder and a natural or tap water sample for their Calcium content. Calcium, along with Magnesium, is one of the major cations present in Tap Water. The concentration of Calcium plus Magnesium is generally referred to as the “hardness” of the water. While both metals are nutrients that are needed for good human health, high concentrations of these cations (Ca$^{2+}$ and Mg$^{2+}$) in water can cause deposits to form in bathrooms and kitchens, and cause the formation of “soap scum.” Therefore, very “hard” water is undesirable for use as Tap Water.

Calcification Due to Hard Water

<table>
<thead>
<tr>
<th>CaCO$_3$ [mg/L]</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 - 60</td>
<td>Soft</td>
</tr>
<tr>
<td>61 - 120</td>
<td>Moderately Hard</td>
</tr>
<tr>
<td>121 - 180</td>
<td>Hard</td>
</tr>
<tr>
<td>180 &lt;</td>
<td>Very Hard</td>
</tr>
</tbody>
</table>

We will use complexometric titrimetry, a form of volumetric analysis, to determine the Calcium content of our samples. In this assay, a standard solution of EthyleneDiamineTetraacetic Acid (EDTA), a metal ion complexing agent, will be added to the analyte solution until complexation of the Calcium Ion is complete. The endpoint of this titration is indicated by a weaker complexing agent, Calmagite, that changes color upon decomplexation.

Complexometric titrations involve the use of complexing agents as titrants for metal cation analytes. Most metal cations react with Lewis Bases, electron-pair donors, to form coordination compounds or complexes. Coordination compounds are substances that contain a complex ion; a species consisting of a central metal atom, a transition metal or Main Group metal, bound to several Ligands. For instance, the coordination compound K$_2$HgI$_4$ contains the complex ion HgI$_4^{2-}$ formed from the Mercuric Ion and four Iodide Ion ligands:
\[
\text{Hg}^{2+}(\text{aq}) + 4 \text{I}^-(\text{aq}) \rightleftharpoons \text{HgI}_4^{2-}(\text{aq})
\]

In this case, the Iodide Ion is acting as a Lewis Base by donating a pair of electrons to the Hg\(^{2+}\) ion, forming a coordinate covalent bond between the Hg and I atoms:

\[
\text{Hg}^{2+} \quad \text{I}^- \quad \text{Hg}^{2+} \quad \text{I}^-
\]

The ligands act as a "complexing agent" for the metal cation. Multidentate ligands, also called chelating agents, provide more than one pair of electrons for complexation, and therefore can form multiple coordinate covalent bonds between the ligand and the metal cation. The resulting chelates are extremely stable; having very large formation constants (K\(_f\)).

EDTA is the most important chelating agent in analytical chemistry. The tetrabasic form of this acid forms complexes with virtually all metal ions. In this form EDTA is a hexadentate ligand; each of the acid oxygens and each of the amine nitrogens can donate one electron pair to the metal. The metal ion is usually held in a one-to-one complex with the EDTA molecule, 6 EDTA to metal coordinate covalent bonds having formed.

**EDTA's Complexing Electrons**

**Metal-EDTA Chelate**
The formation constants for several metal ion-EDTA complexes are listed below:

\[ M^{n+}(aq) + n \text{EDTA}^4-(aq) \rightleftharpoons M\cdot\text{EDTA}^{(n-4)+}(aq) \]  
(Eq. 1)

<table>
<thead>
<tr>
<th>Cation</th>
<th>( K_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(^{2+})</td>
<td>4.9 x 10^8</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>5.0 x 10^{10}</td>
</tr>
<tr>
<td>Sr(^{2+})</td>
<td>4.3 x 10^8</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>5.8 x 10^7</td>
</tr>
<tr>
<td>Mn(^{2+})</td>
<td>6.2 x 10^{13}</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>2.1 x 10^{14}</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>2.0 x 10^{16}</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>4.2 x 10^{18}</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>6.3 x 10^{18}</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>3.2 x 10^{16}</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>2.9 x 10^{16}</td>
</tr>
<tr>
<td>Hg(^{2+})</td>
<td>6.3 x 10^{21}</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>1.1 x 10^{18}</td>
</tr>
</tbody>
</table>

It is important to realize that the electron pairs of the carboxylic acid groups of EDTA are only available to the metal ion when the acid is dissociated. This means that the effectiveness of this complexing agent is strongly affected by pH. At low pH's EDTA will be in an acidic form and will not be an effective complexing agent. However, at high pH's, many metal ions form complexes with Hydroxide Ion, OH\(^-\):

\[ M^{n+}(aq) + n \text{OH}^-(aq) \rightleftharpoons M(\text{OH})_n(s) \]  
(Eq. 2)

Therefore, the effectiveness of EDTA complexation will also be reduced at high pH. For a given chelating agent and metal ion, there will be an optimum pH for the titration which will depend on the p\(K_a\) values for the chelating agent and the formation constants for the metal-hydroxide complexes.

So, in a complexometric titration, a solution containing the free metal ion analyte is titrated with a solution of the chelating agent until all of the metal ions are completely complexed. The endpoint is usually determined using an indicator ligand that forms a colored complex with the free metal ion. This indicating ligand competes less effectively for the metal cation than does the chelating agent. The indicator ligand changes color when it is released from its complex with the metal ion as chelation occurs. This signals the endpoint of the titration.

In this laboratory, we will titrate solutions of Ca\(^{2+}\) with EDTA. For Calcium Ions, this titration has an optimal pH above 8, which we will maintain with an Ammonia/Ammonium Ion buffer. Under these conditions dibasic EDTA (H\(_2\)EDTA\(^5-\)) is the active form of the chelating agent. Thus, the Titration Reaction can be taken as:
\[ \text{Ca}^{2+} (aq) + \text{H}_2\text{EDTA}^2^- (aq) \rightleftharpoons \text{Ca}\cdot\text{EDTA}^2^- (aq) + 2 \text{H}^+ (aq) \] (Eq. 3)

Our Endpoint indicator is Calmagite (3-hydroxy-4-(2-hydroxy-5-methylphenylazo) naphthalene-1-sulfonic acid), a triprotic organic acid which can complex weakly with \text{Ca}^{2+}. Calmagite (\text{H}_2\text{In}^-) is the indicator of choice for several cation titrations and gets its name because it is an excellent indicator for calcium and magnesium; red in the Metal-Indicator form and blue otherwise.

![Calmagite structure](image)

\[ \text{M}\cdot\text{In}^{(n-3)^+} (aq) + \text{H}_2\text{EDTA}^2^- (aq) \rightleftharpoons \text{M}\cdot\text{EDTA}^{(n-4)^+} (aq) + \text{HIn}^2^- (aq) + \text{H}^+ (aq) \] (Red) (Blue) (Eq. 3)

Because Calmagite forms very strong complexes with many transition metals, even traces of these metals may be enough to retain the indicator in the red form. So, very pure (deionized) Water must be used to prevent this problem. Alternatively, masking agents such as \text{CN}^- or \text{S}^- can be added to complex with the transition metals and prevent such an interference.

Unfortunately the Calcium-Calmagite complex has a formation constant that is sufficiently small that a significant fraction of the complex dissociates before the Calcium-EDTA equivalence point is reached. Therefore, the titration endpoint would not represent the equivalence point if Calcium were directly titrated with EDTA using this indicator. This problem can be resolved by adding a small amount of Magnesium Chloride to the EDTA titrant; Magnesium Ion complexes with Calmagite much more strongly than does Calcium. During the initial stages of the titration, the Magnesium will be displaced from the EDTA by Calcium because it forms a less stable EDTA complex (see Table above):

\[ \text{Mg}\cdot\text{EDTA}^2^- (aq) + \text{Ca}^{2+} (aq) \rightleftharpoons \text{Ca}\cdot\text{EDTA}^2^- (aq) + \text{Mg}^{2+} (aq) \] (Eq. 4)

As the Magnesium is displaced, it complexes tightly with the Calmagite indicator. The analyte solution now appears Red. When the Calcium has been completely consumed, the Magnesium will again bind to the EDTA. The excess Magnesium is now titrated to its distinct Calmagite Endpoint. And, as long as the EDTA/Mg system is directly standardized against a Primary Standard such as Calcium Carbonate (\text{CaCO}_3), the required over-titration is accounted for during the standardization procedure.

For our Standardization, Calcium Carbonate (\text{CaCO}_3) will be used as the primary standard. Calcium Carbonate does not dissociate well in water, so it is necessary to aid in the dissociation and shift the equilibrium to the right by addition of Acid:
CaCO\(_3\)(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \quad \text{(Eq. 5)}

2 \text{H}^+(aq) + \text{CO}_3^{2-}(aq) \rightleftharpoons \text{H}_2\text{CO}_3(aq) \rightarrow \text{H}_2\text{O} + \text{CO}_2(g) \quad \text{(Eq. 6)}

This basic complexometric titration is leveraged in commercial kits for determining the hardness of Water.

Test kits for determining the hardness of household water are available at stores that sell water softeners and plumbing supplies. They usually consist of a vessel calibrated to contain a known volume of water, a measuring scoop to deliver an appropriate amount of a solid buffer mixture, an indicator solution, and a bottle of standard EDTA, which is equipped with a medicine dropper. The drops of standard reagent needed to cause a color change are counted. The concentration of EDTA solution is ordinarily such that one drop corresponds to one grain (about 0.065g) of calcium carbonate per gallon of water.

Fundamentals of Analytical Chemistry
Douglas A. Skoog, Donald M. West, F. James Holler
Pre-Lab Calculations

1. A 0.0352 g sample of pure calcium carbonate (100.09 g/mol) was dissolved in acid and titrated to its endpoint with newly made EDTA titrant (~0.010 M) according to the procedure given below. The starting burette volume was 0.10 mL. The ending burette volume was 35.52 mL. Calculate the exact concentration of the EDTA titrant. Show all work.

2. A 0.0456 g sample of an unknown sample was titrated using the EDTA titrant from question 1 and the procedure below. The starting burette volume was 0.05 mL. The ending burette volume was 42.35 mL. Calculate the % calcium oxide (CaO; 56.0774 g/mol) by mass in the sample. Show all work.

3. 100.0 mL of an unknown water sample was titrated using the EDTA from question 1 and the procedure below. The starting volume was 0.25 mL and the ending volume was 20.53 mL. Calculate the concentration of Ca$^{2+}$ in the tap water. Show all work.
Procedure

Preparation of reagents

1. EDTA titrant: Weigh out 2.0 g of ethylenediaminetetraacetic acid disodium salt dehydrate and dissolve it in about 500 mL of deionized water in a 1 L plastic bottle. Add 10 mL of a 1% MgCl₂ solution and 2 mL of 6 M NH₃. Cap the bottle and mix until the solid is dissolved.

2. Ammonia/ammonium buffer: Prepare the buffer solution by dissolving 6 g of NH₄Cl in 100 mL of 6 M NH₃. Store closed in your 100 mL bottle and use in the hood.

Standardization of the EDTA Titrant

1. Weigh out 0.03 g of dried primary standard CaCO₃ into a 250 mL Erlenmeyer flask and record the exact mass to 4 decimal places in your notebook. Dissolve the calcium carbonate by adding 10 mL of deionized water and then adding the least amount of 6 M HCl that is necessary to dissolve the solid. Note that adding a large excess of acid will cause the pH of the titration solution to be too low and the titration to fail. Next, add 10 mL of the buffer and about 30 mL of deionized water to the flask. Swirl to mix.

2. Add 4-5 drops of the calmagite indicator solution. Titrate with the EDTA titrant solution to a blue endpoint with no hint of red. Try doing a quick titration to determine the approximate endpoint first and then do the remaining titrations more slowly as you approach the endpoint. Near the endpoint, add drops one at a time while recording the burette volume after each drop. Allow the solution to stand for a moment after each drop of addition of each drop to ensure completeness of reaction.

3. Repeat the standardization procedure at least three times total (excluding the first quick titration). Calculate the concentration of the EDTA solution after each replicate. Calculate the average [EDTA] and the standard deviation in [EDTA]. Repeat until the precision is better than ± 0.001 M. Use the Q test to eliminate potential outliers. Report these data on the assay sheet. Show one calculation for the EDTA concentration on the back of the assay sheet.

Determination of Calcium in an Unknown Powder

1. Weigh out 0.04 g of a dry unknown powder sample into a 250 mL Erlenmeyer flask and record the exact mass to 4 decimal places in your notebook. Record the sample number in your notebook and on the assay sheet. Dissolve and titrate the sample as above. This endpoint may have a slight purple color to it.

2. Repeat the titration of the unknown at least two more times. Calculate the % CaO by
mass after each replicate. Calculate the average % CaO by mass and the standard deviation in % CaO by mass. Repeat until your precision is better than ± 0.20% by mass. Use the Q test to eliminate potential outliers if needed. Report these data on the assay sheet. Show one calculation for the % CaO by mass on the back of the assay sheet.

**Determination of Calcium in a Water Sample**

1. Pipette 100 mL of an unknown water sample into a 500 mL Erlenmeyer flask. Add 10 mL of triethanolamine (TEA) and 10 mL of the ammonia buffer solution. Swirl to mix. Add 4-5 drops of the calmagite indicator solution. (Do not add it before adding the TEA!) Swirl to mix. Titrate with the EDTA titrant solution to a blue endpoint with no hint of red. This titration may take less volume than the others!

2. Repeat the titration of the tap water two more times. Calculate the concentration of calcium in molarity after each replicate, the average calcium concentration (in M and mg/L) and the standard deviation in calcium (in M and mg/L). Report these data on the assay sheet. Show one set of calculations for the concentration of calcium in M and the unit conversion to mg/L on the back of the assay sheet.